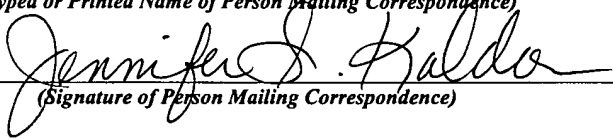
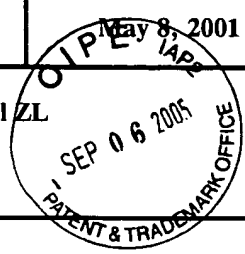


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TPW 1764

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Application No. 09/851,264	Filing Date May 8, 2001	Examiner Tam M. Nguyen	Customer No. 23455	Group Art Unit 1764
Invention: Colloidal ZL				
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Johannes Petrus Verduijn

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Tam M. Nguyen

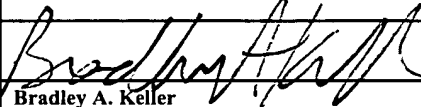
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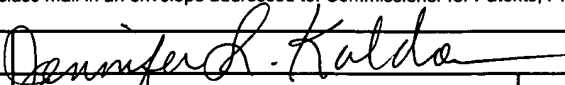
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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

95304800.6

Der Präsident des Europäischen Patentamts;
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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**Blatt 2 der Bescheinigung
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Applicant(s):
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Bezeichnung der Erfindung:
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Titre de l'invention:
Zeolites and processes for their manufacture

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Case No. 95M014

"Zeolites & Processes for their Manufacture"

This invention relates to zeolites of structure type LTL, to processes for the manufacture of such zeolites, and to the use of the zeolites as catalysts and catalyst bases. The zeolites have a 12 membered ring structure with pore dimensions of 0.55 to 0.72 nm.

An example of a zeolite of LTL structure type is zeolite L, and processes for the manufacture of zeolite L are described in U.S. Patent No. 3216789, EP-A-219354, and EP-A-595465, the disclosures of all of which are incorporated by reference herein. The two European patent applications, which have extensive prior art discussions to which the reader is referred for more background, and the U.S. Patent list the significant X-ray diffraction data for crystalline zeolite L and give its formula in terms of moles of oxides as

$0.9 \text{ to } 1.3 \text{ M}_{2/n}\text{O}:\text{Al}_2\text{O}_3:5.2 \text{ to } 6.9:\text{SiO}_2:y\text{H}_2\text{O}$,
where M represents an exchangeable cation of valence n, and y represents a value within the range of from 0 to about 9. In Proceedings of the 9th International Zeolite Conference, Ed. von Ballmoos et al, 1993, p. 297, Xianping Meng et al describe the effect of varying crystallization conditions and reactant ratios on a process for the manufacture of ultrafine (particle size about 30 nm) zeolite L.

Products of such a small particle size have advantages over larger particle size products, such as those produced by the procedure of U.S. Patent No. 3216789, when used as a catalyst, or catalyst base, for reactions involving hydrocarbon conversions because of their enhanced ratio of surface area to mass, high diffusion rates and reactivities, and resistance to deactivation by pore plugging and surface contamination. For similar reasons they have advantages in hydrocarbon separations, and are also valuable as starting materials in the manufacture of supported zeolite layers, especially membranes, as described in WO 94/25151, the disclosure of which is also incorporated herein by reference. For the latter purpose, a zeolite having a particle size, whether in the form of agglomerates or single crystals, of at most 100 nm, and advantageously at most 75 nm, is normally required since the zeolite layer is formed by deposition from a colloidal suspension onto a support; if for any reason the suspension is not stable it is unsuitable for the purpose. Although EP-A-595465 describes the product of the inventive process, in which ammonia is used as a co-solvent to water in the zeolite synthesis mixture, as being in mono-crystalline form, and refers to carrying out the hydrothermal treatment at a temperature in the range of 70 to 160°C to yield a product having crystallites of diameter less than about 30 nm, it appears from the description and micrograph in

the Application that the product consists of larger agglomerates of the nanocrystals incapable of forming a colloidal suspension.

It has now surprisingly been found that if a synthesis mixture as described in U.S. Patent No. 3216789 is subjected to heat treatment at a temperature below 100°C a colloidal suspension of zeolite results.

The present invention accordingly provides a process for the manufacture of a colloidal suspension of an LTL zeolite, wherein a synthesis mixture having a composition, given in terms of molar proportions with the solid components being calculated in terms of their oxides, in the range:

$K_2O/(K_2O + Na_2O)$	from 0.33 to 1:1
$(K_2O + Na_2O)/SiO_2$	from 0.35 to 0.5:1
SiO_2/Al_2O_3	from 10 to 28:1
$solvent/(K_2O + Na_2O)$	from 15 to 25:1

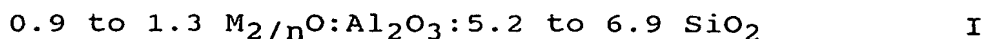
is subjected to thermal treatment at a temperature below 100°C for a time sufficient to form a colloidal suspension of an LTL zeolite for the solvent.

Advantageously, the solvent is water, but the presence of a co-solvent, e.g., ammonia, is not excluded, in which case its molar proportion is included in the specified range.

The invention further provides a process for the manufacture of an LTL zeolite of particle size at most 100 nm, wherein the colloidal suspension prepared as

described above is washed with water to a pH within the range of 9 to 12, advantageously 10 to 11, and if desired cation exchanged, dried and, if desired, calcined.

Advantageously, the resulting zeolite is one having a composition of Formula I



wherein M is an exchangeable cation of valence n.

The process of the invention provides either individual crystals or agglomerates which form a colloidal suspension, i.e., the suspension produced directly, or by washing, is a stable one.

A stable suspension is one in which settlement does not take place, or one in which any settlement that takes place does so so slowly as to be insignificant over the relevant timescale. Such a suspension is referred to herein as colloidal.

As described above, the zeolites of the invention are primarily aluminosilicates, and will be described herein as such. It is, however, within the scope of the invention to replace aluminium wholly, though preferably only partly, with gallium, and partly with boron, iron or other trivalent elements, and silicon may similarly be replaced by germanium or phosphorus. It is also within the scope of the invention to include cations other than potassium and sodium in the synthesis mixture.

The sources of the various elements required in the final product may be any of those in commercial use or

described in the literature, as may the preparation of the synthesis mixture.

For example, the source of silicon may be a silicate, e.g., an alkali metal silicate, or a tetraalkyl orthosilicate, but there is preferably used an aqueous colloidal suspension of silica, for example one sold by E.I. du Pont de Nemours under the trade name Ludox. Ludox HS-40 is a sodium-containing product, while AS-40 contains very little sodium.

The source of aluminium is preferably $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, dissolved in alkali. Other aluminium sources include, for example, a water-soluble aluminium salt, e.g., aluminium sulphate, or an alkoxide, e.g., aluminium isopropoxide.

The potassium source is advantageously potassium hydroxide and the sodium source, if present, is advantageously also the hydroxide.

The synthesis mixture is conveniently prepared by mixing two solutions, one containing the potassium and aluminium sources, and the other the silica source, each containing water in a quantity such that, on mixing, the required molar proportions result.

Crystallization is effected, either under static conditions or with moderate stirring, and, if desired, under reflux.

Thermal treatment, otherwise known as elevated temperature ageing, at a temperature in the range of

from 40 to 97°C is convenient; advantageously from 50 to 95°C and preferably from 60 to 85°C. Although crystallization times are normally described in the prior art as being longer at lower temperatures, it has been surprisingly found that, while times from 48 to 500 hours may be used, even at temperatures at the lower end of the present range, times up to 84 hours may suffice. A lower temperature in general gives a smaller particle size zeolite, if other conditions remain constant. By appropriate choice of temperature, agglomerates of greatest dimensions in the range of 25 nm to 100 nm may be obtained, with good uniformity of particle sizes.

The colloidal suspension, or the crystals obtainable from the suspension, produced by the processes described above may be used in a number of applications including the manufacture of thin films on substrates, in which application the crystals may provide a growth-enhancing layer, or as the base of the film itself, for example by multiple in-situ crystallization. More especially, however, according to the present invention, the nanometric sized agglomerates may be used as seeds in the manufacture of zeolite L.

As noted in U.S. Patent No. 3216789, if a synthesis mixture has a composition having other than a low alkalinity it tends to produce either a zeolite other than zeolite L, zeolite L contaminated with other zeolites or with amorphous material, or an amorphous

product only. For example, too low an alkalinity results in zeolite W formation, or in zeolite L contaminated with zeolite W.

It has previously been proposed, in U.S. Patent No. 5330736, to manufacture zeolite L using as seeding gel an amorphous aluminosilicate seeding gel which does not contain zeolite L. The gel is stated to be one which, if heated to 100°C on its own would produce zeolite Y. In the patent, a number of earlier U.S. patents are discussed which are stated to mention the possibility of seeding zeolite L-producing synthesis mixtures with zeolite L seeds. Examples 12 and 13 of U.S. Patent No. 4657749, one referred to in Patent No. 5330736, describe a seeding process, in which seeds of an unspecified particle size zeolite L are used. In a comparison example in U.S. Patent No. 5330736, a preformed crystalline zeolite L of unspecified particle size was used to seed a zeolite L-forming synthesis mixture, with a zeolite T-contaminated zeolite L product resulting.

It has now been found that colloidal zeolite L seeds may successfully be used to promote the formation of zeolite L from a synthesis mixture, even if that mixture is one which, in the absence of colloidal seeds, would give a product other than pure zeolite L.

The present invention accordingly provides a process for the manufacture of an LTL zeolite which comprises

forming a synthesis mixture having a composition, given in terms of molar proportions with the solid components calculated in terms of their oxides, in the range:

$K_2O/(K_2O + Na_2O)$	from 0.60 to 1:1
$(K_2O + Na_2O)/SiO_2$	from 0.18 to 0.36:1
SiO_2/Al_2O_3	from 5 to 15:1
$H_2O/(K_2O + Na_2O)$	from 25 to 90:1

and also containing seed crystals of an LTL zeolite of particle size at most 100 nm, and subjecting the seed-containing synthesis mixture to a hydrothermal treatment at a temperature and for a time sufficient to form an LTL zeolite.

Advantageously, the LTL zeolite is zeolite L.

It has surprisingly been found that very small proportions of the colloidal zeolite seeds are effective to promote crystallization of the desired zeolite from the synthesis mixture without contamination with other crystalline zeolite forms or amorphous material. The uniformity of size of the resulting particles is good.

In contrast to the above-mentioned comparative example in U.S. Patent No. 5330736, which employed about 0.5% by weight of seeds, based on the total synthesis mixture, the process of the present invention is effective with ppm proportions of colloidal seeds, e.g., from 0.005% by weight, based on the weight of the total synthesis mixture, advantageously from 0.015 to 0.05%, conveniently about 0.025%. Although it is within the

scope of the invention to employ a greater proportion, no technical advantage appears to result.

The seeds, prepared conveniently as described above, advantageously have a particle size within the range of from 25 nm to 100 nm, preferably from 60 to 80 nm.

Hydrothermal treatment is advantageously carried out at a temperature of 100°C to 180°C, preferably from 150°C to 175°C, for a time advantageously within the range of 4 to 200 hours, preferably for from 20 to 80 hours, advantageously under autogenous pressure.

The thermal treatment may be carried out under static conditions or with moderate stirring.

The sources of the various components of the synthesis mixture, other than the seeds, may be as described with reference to the first embodiment of the invention, the formation of the colloidal LTL zeolite suspension, while the seeds are advantageously the product of the first embodiment of the invention.

By using the seeding process of the invention, zeolite L formation is promoted in, for example, synthesis mixtures that are prone to yield zeolite T or W product.

The invention further provides the use, in a process for the hydrothermal treatment of a synthesis mixture for Zeolite L, of a temperature below 100°C to obtain a colloidal suspension of Zeolite L, or to obtain particles

of zeolite L having a greatest dimension of at most 100 nm.

The invention further provides the use, in the hydrothermal treatment of a zeolite-forming synthesis mixture, of seeds of zeolite L having a greatest dimension of at most 100 nm, to promote the crystallization from the synthesis mixture of a zeolite L-containing product, advantageously a product consisting essentially of zeolite L, and preferably a pure zeolite L product. By increasing the concentration of colloidal zeolite L seeds the product particle size may be reduced, the conditions being otherwise kept constant.

The zeolite L produced by the second aspect of the invention, if required after washing, cation exchange and/or calcining, is suitable for use as a catalyst in numerous hydrocarbon conversions or is effective in hydrocarbon separations or adsorptions. The zeolite L material may be used, alone or in admixture with other zeolites, in particulate form or in the form of a layer on a support, especially as a membrane. Hydrocarbon conversions include, for example, cracking, reforming, hydrofining, aromatization, alkylation, isomerization and hydrocracking. The zeolite L may also be used as a catalyst base, especially useful in aromatization processes, e.g., for a Group VIII metal, e.g., palladium or platinum, as described in EP-A-219354.

The following examples illustrate the invention.

Comparison Example A

Example 1 of U.S. Patent No. 3216789 was repeated.

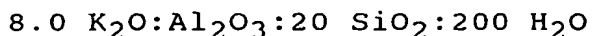
The following two solutions were prepared:

<u>Solution A</u>	<u>parts by weight</u>
KOH pellets, 87.4% purity (Baker)	53.17
Al(OH) ₃ , 98.5% purity (Alcoa)	8.20
H ₂ O, deionized	57.19

The potassium and aluminium sources were mixed with the water which was boiled until a clear solution resulted. After cooling to room temperature, any water loss was corrected.

<u>Solution B</u>	<u>parts by weight</u>
SiO ₂ , Ludox HS40, 40% SiO ₂ by weight	155.54
H ₂ O, deionized	23.13

Solution A was quantitatively added to Solution B with stirring. The resulting synthesis mixture had a molar composition of



A portion of the synthesis mixture was transferred to a glass liner, which was placed in a stainless steel autoclave. The autoclave was placed in an oven, which was then heated from room temperature to 100°C over a 2 hours period, and maintained at that temperature for 169 hours.

After cooling, the autoclave was opened and the contents of the liner were examined. A product had settled on the bottom leaving a clear mother liquor. The...

product was washed several times with water to reach a pH of 10.2, and then dried in an oven.

X-ray diffraction (XRD) showed a pattern characteristic of zeolite KL. Scanning electron microscopy (SEM) shows spherical agglomerates with an average size of 125 nm, as shown in Fig. 1.

Examples 1 to 3

The procedure of Comparison Example A was followed up to the preparation of the synthesis mixture, but various samples of the resulting mixture were thermally treated at the temperatures and for the times shown in Table 1 below. Crystallization was effected in polypropylene vessels under reflux conditions. The resulting reaction mixtures were washed with water to a pH of between 10 and 11, and kept in the last wash water. Separation of the product from the final wash waters was effected by high speed centrifugation. In Example 3, a sample was taken from the reaction mixture after 68 hours heating. A portion of this sample and of each of the washed slurry products of the completed experiments was dried and used to obtain X-ray diffraction and SEM data. The XRD and SEM results show that the product of Example 3 was the same after 68 hours as after the complete 164 hour treatment.

Table 1
Effect of Crystallization Temperature
on SEM particle size

Example	Crystallization Temp. °C	Time, hours	XRD	Particle Size, nm by SEM
1	92.5	408	KL - peak broadening	≈ 75
2	82.5	432	KL - peak broadening	≈ 50
3a	72.5	68	KL, extremely	≈ 30
3b	72.5	164	weak pattern	≈ 30

The washed reactor slurries of Example 1 to 3 were transferred to plastics containers and left undisturbed for 7 days. The suspended KL products showed no tendency to settle on the container bases. All Examples 1 to 3 products showed a very weak but still recognizable XRD pattern of KL, with no amorphous halo whose presence would show contamination by amorphous by-products. A TEM micrograph of the Example 3 product is shown in Fig. 2.

The toluene adsorption properties of the products of Examples 1 to 3 were compared with those of a highly crystalline (as shown by XRD) standard KL product. The results are shown in Table 2.

Table 2

Toluene Capacity, wt %

Material	Micropore*	Macropore
Standard KL	9.95	0.24
Example 1	8.71	13.31
Example 2	10.65	10.10
Example 3	10.35	10.00

* Wt% Toluene absorbed after 60 minutes desorption with N₂, 30°C

The results confirm the crystallinity of the products of Examples 1 to 3. Their increased macropore capacity indicates that there are small voids between individual nanometer-sized KL particles.

Example 4

The following two solutions were prepared:

<u>Solution A</u>	<u>parts by weight</u>
KOH pellets, 87.4% purity (Baker)	30.31
Al(OH) ₃ , 98.5% pellets (Alcoa)	15.84
H ₂ O, deionized	75.58

The potassium and aluminium sources were mixed with the water which was boiled until a clear solution resulted. The solution was cooled to room temperature and water loss made up.

<u>Solution B</u>	<u>parts by weight</u>
SiO ₂ , Ludox HS40	150.24
H ₂ O, deionized	115.20
Zeolite L seeds, 75 nm, 5.49 wt %	
solids in water	1.7884

The water was added to the colloidal silica, and the resulting liquids mixed in a blender. The seed suspension was added to the blender contents, and mixed for 30 seconds. Then Solution A was added and mixed for a further 3 minutes, a thickening gel being obtained. The seeds used were obtained as described in Example 1.

The molar composition of the synthesis mixture was:

2.36 K₂O:Al₂O₃:10 SiO₂:162 H₂O

with 252 ppm (0.025%) by weight seeds, based on the total weight of mixture.

326.70 g of synthesis mixture were transferred to a 300 ml stainless steel autoclave, which was placed in an oven at room temperature. The oven was heated over the course of 4 hours to 175°C and maintained at that temperature for 66 hours.

After cooling, the product was washed 5 times with 750 ml of water, to reach a wash water pH of 9.6. The product was dried at 120°C; the yield was 50.9 g.

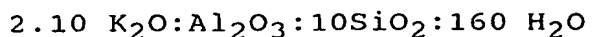
SEM showed a product consisting of cylindrical crystallites with an average length of 0.6 μm, l/d ratio 1.7, with flat basal planes; SEM indicated that the crystal morphology had all the characteristics of a

cylindrical KL species. Figs. 3 and 4 show SE micrographs at magnifications of 10,000 and 40,000 respectively.

Example 5 and Comparison Example B

In these examples, the effect of colloidal seeds on the product of a synthesis mixture of alkalinity lower than that of Example 4 was examined.

Two synthesis mixtures, both of molar composition:

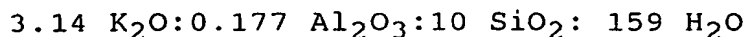


were prepared, that of Example 5 containing in addition 0.075% by weight of seeds produced as described in Example 1, that of Comparison Example B containing no seeds. Both mixtures were hydrothermally treated in stainless steel autoclaves for 80 hours at 150°C.

The product of Example 5 was excellently crystalline and pure zeolite L, while that of Comparison B consisted mainly of zeolite W and amorphous material.

Example 6

A synthesis mixture with a molar composition of



was prepared. The $\text{K}_2\text{O}:\text{Al}_2\text{O}_3$ ratio of this synthesis mixture was such that if hydrothermally treated on its own a zeolite L heavily contaminated with zeolite T and amorphous material would result. The mixture was, however, seeded with 255 ppm (0.025%) by weight 75 μm KL seed crystals, prepared as described in Example 1.

The mixture was treated for 80 hours at 170°C in a stainless steel autoclave, washed with water to pH 9.5, and dried at 120°C. The product was pure zeolite KL. SEM showed a product of disk-shaped crystals with flat basal planes ("hockey puck" type crystals). Figs. 5 and 6 show SE micrographs at magnifications of 10,000 and 40,000 respectively.

CLAIMS:

1. A process for the manufacture of a colloidal suspension of an LTL zeolite, wherein a synthesis mixture having a composition, given in terms of molar proportions with the solid components being calculated in terms of their oxides, in the range:

$K_2O/(K_2O + Na_2O)$	from 0.33 to 1:1
$(K_2O + Na_2O)/SiO_2$	from 0.35 to 0.5:1
SiO_2/Al_2O_3	from 10 to 28:1
solvent/ $(K_2O + Na_2O)$	from 15 to 25:1

is subjected to thermal treatment at a temperature below 100°C for a time sufficient to form a colloidal suspension of an LTL zeolite.

2. A process as claimed in claim 1, wherein thermal treatment is carried out at a temperature within the range of from 60° to 97°C.

3. A process as claimed in claim 1 or claim 2, wherein thermal treatment is carried out for a time within the range of from 48 to 500 hours.

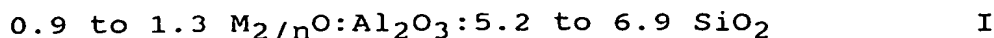
4. A process as claimed in any one of claims 1 to 3, wherein thermal treatment is carried out for a time of at most 84 hours.

5. A process as claimed in any one of claims 1 to 4, wherein the solvent is water.

6. A process as claimed in any one of claims 1 to 4, wherein the colloidal suspension is washed with water until the wash water has a pH of from 9 to 12, if

desired the zeolite is cation exchanged, and if desired calcined.

7. A process as claimed in any one of claims 1 to 6, wherein the resulting zeolite has a composition of the Formula I



wherein M represents an exchangeable cation of valence n.

8. Zeolite L of particle size less than 100 μm obtainable, and preferably obtained, by a process as claimed in any one of claims 1 to 7.

9. A process for the manufacture of an LTL zeolite which comprises forming a synthesis mixture having a composition, given in terms of molar proportions with the solid components calculated in terms of their oxides, in the range:

$\text{K}_2\text{O}/(\text{K}_2\text{O} + \text{Na}_2\text{O})$ from 0.60 to 1:1

$(\text{K}_2\text{O} + \text{Na}_2\text{O})/\text{SiO}_2$ from 0.18 to 0.36:1

$\text{SiO}_2/\text{Al}_2\text{O}_3$ from 5 to 15:1

solvent/ $(\text{K}_2\text{O} + \text{Na}_2\text{O})$ from 25 to 90:1

and also containing seed crystals of an LTL zeolite of particle size at most 100 nm, and subjecting the seed-containing synthesis mixture to a hydrothermal treatment at a temperature and for a time sufficient to form an LTL zeolite.

10. A process as claimed in claim 9, carried out at a temperature within the range of 100°C to 180°C.

11. A process as claimed in claim 9 or claim 10, carried out for a time within the range of from 4 to 200 hours.

12. A process as claimed in any one of claims 9 to 11, wherein from 0.005% by weight of seeds is employed, based on the weight of the synthesis mixture.

13. A process as claimed in any one of claims 9 to 12, wherein the seeds have a particle size within the range of 60 to 80 μm .

14. A process as claimed in any one of claims 9 to 13, wherein the solvent is water.

15. A process as claimed in any one of claims 9 to 14, wherein the resulting zeolite is washed with water until the wash water has a pH of from 9 to 12, if desired the zeolite is cation exchanged, and if desired calcined.

16. Zeolite L whenever prepared by a process as claimed in any one of claims 7 to 15.

17. The product of claim 16 in the form of a layer on a support.

18. The use, in a process for the thermal treatment of a synthesis mixture for Zeolite L, of a temperature below 100°C to obtain a colloidal suspension of Zeolite L, or to obtain particles of zeolite L having a greatest dimension of at most 100 nm.

19. The use, in the hydrothermal treatment of a zeolite-forming synthesis mixture, of seeds of zeolite L having a greatest dimension of at most 100 nm, to promote

the crystallization from the synthesis mixture of a zeolite L-containing product, advantageously a product consisting essentially of zeolite L, and preferably a pure zeolite L product.

20. The use of zeolite L obtainable or obtained by the process of any one of claims 9 to 13 in particulate or layer form, in hydrocarbon conversion, adsorption or separation.

EXXON CHEMICAL PATENTS, INC.

Case No. 95M014

ABSTRACT

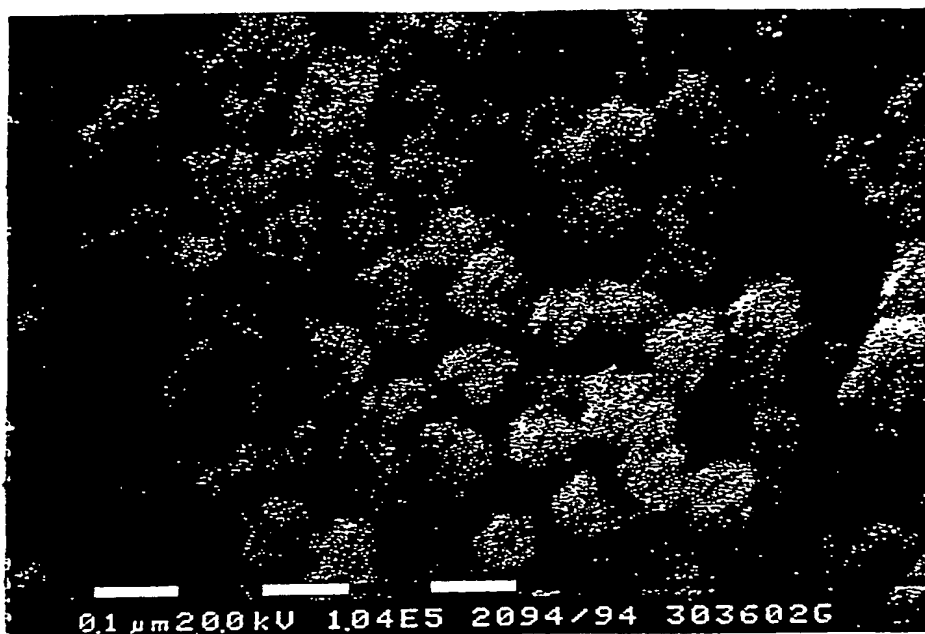
"Zeolites & Processes for their Manufacture"

Low temperature hydrothermal treatment of a zeolite L-producing mixture produces colloidal suspensions of the zeolite.

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Attachment 1 : Comparative SEM Micrographs
Magnification 104,000 *

DUPLICATION US 3216789



Average particle size ~ 125 nm

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FIG. 1.

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45.0K C.2.2.1

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FIG. 2

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Attachment 1 : SEM Micrographs of cylindrical KL synthesized in the presence of ppm quantities of colloidal KL as seed

10,000 *



Fig. 3.

40,000 *

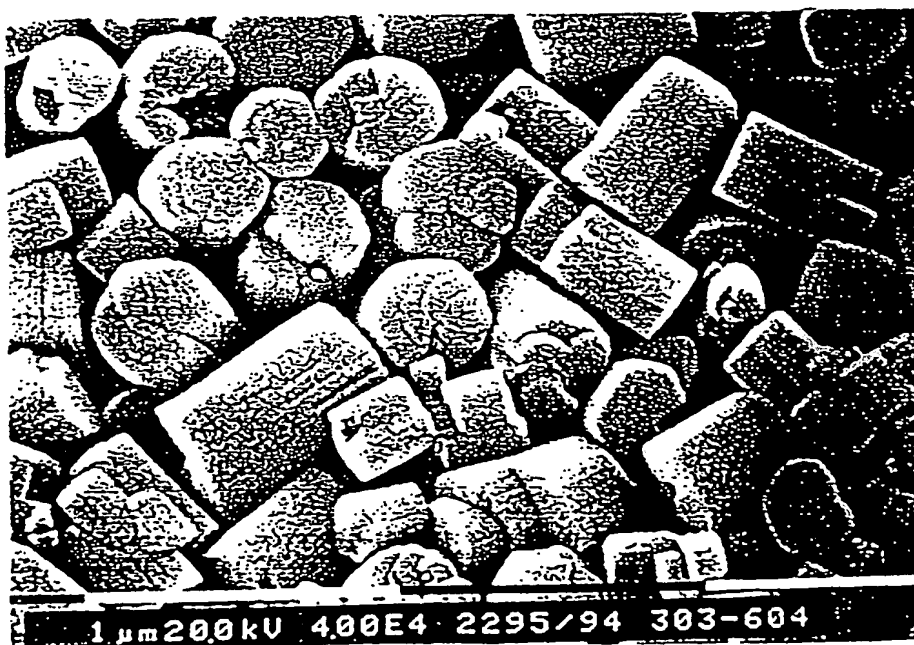


Fig. 4

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Attachment 2 : SEM Micrographs of hockey puck type KL synthesized in the presence of ppm quantities of colloidal KL as seed

10,000 *

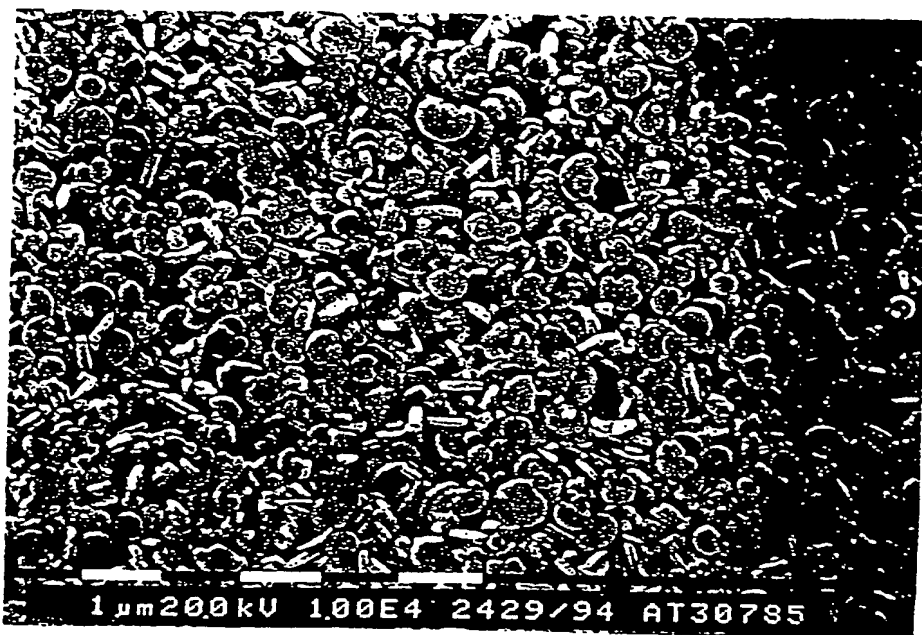


Fig. 5

40,000 *



Fig. 6

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